REDUCED EMISSIONS TRANSPORTATION FUEL

The invention relates to reduced emissions transportation fuels, formulated to reduce emissions of toxics, hydrocarbons (VOCs) and NO_x. More particularly, the invention relates to transportation fuels that are formulated to reduce emissions of toxics, hydrocarbons (VOCs) and NO_x, and have reduced sulfur content.

BACKGROUND OF THE INVENTION

There are many challenges for U.S. refiners to produce fuels that comply with environmental regulations and meet vehicle performance requirements. Federal and State Governments have regulated gasoline properties for many years. Generally, these regulations were developed to meet air quality goals. In 1990, the Federal Government issued the Clean Air Act Amendments, which required significant changes to gasoline used in certain areas of the United States.

Beginning January 1, 1998, refiners had to certify their reformulated gasolines using the EPA Complex Model, a computer model that predicts emissions performance. The properties used in the Complex Model to predict emissions performance are: methyl tert-butyl ether (MTBE) (wt.% oxygen), ethyl tert-butyl ether (ETBE) (wt.% oxygen), Ethanol (wt.% oxygen), Methanol (wt.% oxygen), tert-amyl methyl ether (TAME) (wt.% oxygen), sulfur (ppm), Reid Vapor Pressure (psi), 50% D-86 distillation point (°F) or E200(%), 90% D-86 distillation point (°F) or E300(%), aromatics (vol%), olefins (vol%), and benzene (vol%).

U.S. Patents No. 5,288,393, 5,593,567, 5,653,866, 5,837,126 and 6,030,521 indicate that the primary factor effecting NO_x emissions is Reid Vapor Pressure (RVP),

with the 10% D-86 Distillation Point and Olefins content being of secondary importance. It is reported that since reductions in 10% D-86 Distillation Point are often unacceptable for performance reasons, olefins content is generally to be used as the secondary variable in decreasing NO_x emissions. These U.S. Patents report that a Reid Vapor Pressure of less than 8.0 psi and an olefins content not exceeding 15% by weight are preferred for NO_x emissions reductions. These U.S. Patents also reports that 50% D-86 and distillation points not exceeding 215 °F are preferred for reducing hydrocarbon and carbon monoxide emissions.

An olefins content of less than 15% by weight is generally not difficult to achieve in high octane blends, such as 93 octane gasoline, since these fuels are generally low in olefins due to the components used to produce them. However, it is more difficult to achieve this olefins content in lower octane fuels, such as 87 octane, because of the high olefins content of the components used to produce these fuels.

An additional issue facing refiners is the pending implementation of the EPA Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements. Beginning in 2004, refiners must produce gasoline that averages 120ppm sulfur with a batch limit of 300ppm. In 2005, gasoline sulfur levels must average 90ppm with a 300ppm cap, and in 2006, these limits are a 30ppm average with an 80ppm cap.

It is desirable to produce transportation fuels that meet the emissions reductions requirements determined using EPA Complex Model and can be produced using components having a high concentration of olefins. It is further desirable to produce transportation fuels that meet the emissions reductions requirements using the EPA Complex Model and have reduced sulfur content.

SUMMARY OF THE INVENTION

The current invention provides transportation fuels that meet the emissions requirements for toxics, VOC and NO_x as determined using the EPA Complex Model. Reductions in NO_x emissions are achieved primarily by controlling the 90% D-86 distillation point, olefins content, aromatics content and sulfur content. Reductions in VOC emissions are achieved primarily by controlling Reid Vapor Pressure and secondarily by controlling aromatics content. Reductions in toxics emissions is achieved primarily by controlling aromatics and benzene content, 90% D-86 distillation point and the use of oxygenates. Transportation fuels according to the current invention can have olefins content from about 0- 25% by weight, preferably about 15 -25%. Sulfur content in transportation fuels according to the current invention is less than about 300ppm, preferably less than about 120ppm, and most preferably less than about 80ppm. Reduced sulfur content in transportation fuels according to the current invention allows higher olefins content and higher 50 and 90% D-86 distillation points than would otherwise be required for meeting emissions reduction requirements.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to transportation fuels blended to comply with the requirements for emissions reduction, determined using the EPA Complex Model. The EPA Complex Model uses the following parameters for estimating NO_x, VOC and toxics emissions: methyl tert-butyl ether (wt.% oxygen), ethyl tert-butyl ether (wt.% oxygen), ethanol (wt.% oxygen), methanol (wt.% oxygen), tert-amyl methyl ether (wt.% oxygen),

sulfur (ppm), Reid Vapor Pressure, D-86 50% distillation point (°F) or E200 (%), D-86 90% distillation point (°F) or E300 (%), aromatics (volume %), olefins (volume %) and benzene (volume %). As defined in the complex model, the wt. % oxygen contributed by an oxygenating component, such as methyl tert-butyl ether, is the percent oxygen content in the fuel blend on a total weight basis. As defined in the EPA Complex Model, the E200 (%) and E300 (%) are the percentages of a fuel that vaporizes at 200°F and 300°F respectively.

Fuels according to the current invention were blended to comply with the requirements for reductions in NO_x emissions by controlling at least one of the following properties from the EPA Complex Model: the 90% D-86 distillation point, olefins content, aromatics content and sulfur content, as indicated in the tables. VOC emissions are controlled by controlling Reid Vapor Pressure and aromatics content. Toxics emissions are controlled by controlling aromatics and benzene content, 90% D-86 distillation point and the use of oxygenates.

According to one embodiment, fuels of the current invention have octane ratings of 94 (R+M)/2 or lower, preferred octane ratings being 87, 93 and 94. The 50% D-86 distillation point of fuels according to this embodiment of the invention is less than about 235°F, preferably from about 215°F to about 235°F. The 90% D-86 distillation point of fuels according to this embodiment of the invention is less than about 360°F, preferably from about 315°F to about 360°F. Olefins content of fuels according to this embodiment of the invention is less than about 25%, preferably from about 15% to about 25%. Aromatics content of fuels according to this embodiment of the invention is less than about 47%, preferably from about 20% to about 40%. Sulfur content for fuels according

to this embodiment of the invention is less than about 300ppm. Preferably, the sulfur content of fuels according to this embodiment of the invention is about 120 ppm or less, more preferably about 80 ppm or less.

Fuels according to this embodiment of the invention fall into two basic categories, oxygenated and non-oxygenated fuels. For the purposes of the invention, non-oxygenated fuels are those fuels that contain less than 0.1% oxygen by weight. In preferred embodiments, oxygen can be introduce by using oxygenating components, such as: ethyl tert-butyl ether (EtBE), methyl tert-butyl ether (MtBE), tert-amyl methyl ether (TAME), ethanol and methanol. Selection of a particular oxygenating component is within the purview of an individual skilled in the art.

It will be recognized that the examples presented here are for illustrative purposes only and should not be construed as placing a limitation upon the scope of the invention. Further the development of procedures for blending hydrocarbon streams to achieve fuels having the desired content of the several components listed in **Tables 1, 2, 3** and **4** can be carried out by one skilled in the art, without undue experimentation. Methods for developing procedures for blending hydrocarbon streams to produce fuels having the desired content of aromatics, olefins, etc., as well as 10, 50 and 90% D-86 distillation points include, but are not limited to, linear programming and non-linear programming. Those skilled in the art will recognize that the fuel blends of the current invention are not limited to a particular method of developing blending procedures to produce them.

Tables 1, 2, 3 and **4** show examples of transportation fuels of various octane ratings according to the current invention. The examples shown in **Tables 1, 3** and **4** are oxygenated fuels. **Table 2** shows non-oxygenated fuels. The values presented for olefins

and aromatics content in **Tables 1, 2, 3** and **4** are not corrected for content of oxygenates. **Tables 5, 6,** 7 and **8** show emissions of toxics, VOCs and NO_x for the fuels shown in **Tables 1, 2, 3** and **4**, and reductions versus emissions for an industry average baseline fuel calculated using the EPA Complex Model. The industry average baseline fuel has the following properties: 339ppm sulfur, 1.53% benzene, 8.7psi RVP, 87.3(R+M)/2, 128F T10, 218F T50, 330F T90, 32% aromatics, 9.2% olefins and 58.8% saturates. These values represent average 1990 nationwide (excluding California) gasoline composition.

The values for aromatics, benzene, olefins and sulfur content reported in **Tables 1, 2, 3** and **4** were corrected for oxygen content prior to being used to calculate emissions for the example fuels in the EPA Complex Model.

The data from **Tables 5, 6,** 7 and **8** show a decrease in emissions of toxics, VOCs and NO_x versus the baseline fuel. **Table 6** shows emissions for non-oxygenated fuels. **Tables 5,** 7 and **8** show emissions for oxygenated fuels according to a preferred embodiment. Emissions values for toxics, NO_x and VOCs is reported in mg/mile. The values for percentage reduction are calculated versus an industry average baseline fuel. In addition, all fuels according to this embodiment meet the EPA requirement of not more than 300 ppm sulfur. Non-oxygenated fuels according to the current invention show a reduction in toxics emissions of up to about 28%, a reduction in NO_x emissions of up to about 14%, and a reduction in VOC emissions of up to about 22% versus an industry average baseline fuel. Oxygenated fuels according to the current invention show a reduction in toxics emissions of up to about 40%, a reduction in NO_x emissions of up to

about 16%, and a reduction in VOC emissions of up to about 36% versus an industry average baseline fuel.

According to another embodiment, the current invention provides a blend stock for use in blending with oxygenates to produce an oxygenated fuel. Blend stocks according to this embodiment have an octane rating of at least 83.5 and are suitable for blending with oxygenates to produce a reduced emissions transportation fuel. Blend stocks according to this embodiment of the invention have a 50% D-86 distillation point of less than about 232°F, preferably from about 215°F to about 232°F, and a 90% D-86 distillation point less than about 360°F, preferably from about 315°F to about 360°F. The aromatics content of blend stocks according to this embodiment of the invention is less than about 33%, preferably from about 14% to about 33%. The olefins content of blend stocks according to this embodiment of the invention is less than about 21%, preferably from about 15% to about 21%.

Blend stocks according to this embodiment of the invention are blended with an oxygenating component to produce an oxygenated transportation fuel. Such oxygenating components include ethyl tert-butyl ether (EtBE), methyl tert-butyl ether (MtBE), tert-amyl methyl ether (TAME), ethanol and methanol.

A preferred embodiment provides a blend stock having an octane rating of 83.5. According to this embodiment, the blend stock is blended with ethanol to produce a transportation fuel having an octane rating of from about 87 to about 90. **Table 9** shows examples of fuels produced from a blend stock according to this preferred embodiment, blended with ethanol. **Table 10** shows emissions data for the examples in **Table 9**. Fuels produced from blend stocks according to this embodiment show a reduction in toxics

emissions of up to about 26%, a reduction in NO_x emissions of up to about 10%, and a reduction in VOCs of up to about 25%. Reductions in emissions were determined versus an industry standard baseline fuel.